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To study the effect of catalyst on graphitization of anthracene and phenanthrene by X-ray diffraction

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Abstract : Some partially pyrolyzed aromatic organic composite samples have been studied by X-ray diffraction method. Interlayer spacing, Miller indices, ralative intensity and integral widths of the diffraction lines have been calculated. The interlayer spacing is found to decrease as the amount of catalyst is increased The result is explained as an indication of increasing degree of graphitizability with the addition of $AlCl_3$ as catalyst.

Keywords : Catalyst, graphitization, interlayer spacing

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1. Introduction

The history of X-ray studies on carbon and graphite is closely linked with the development of theories and experiments in the field of X-ray diffraction. Graphite is one of the first substances investigated by X-ray diffraction. Ewald *et al* [1] demonstrated the hexagonal symmetry of a graphite single crystal by means of a Laue photograph and concluded from a qualitative interpretation that the number of nearest neighbours should be different from that in diamond. Bragg *et al* [2] measured the first interlayer spacing. Debye and Scherrer [3,4] and Hull [5] made the first attempt to determine the crystal structure from powder diagrams. However, Debye and Scherrer found the correct structure of the graphitic layers but gave a wrong sequence for the layer stacking, whereas Hull found the right sequence for the layer stacking but with a wrong structure for the layers. The correct structure of the hexagonal form was first published by Hassel and Mark [6], followed shortly by Bernal [7]; the structure of the rhombohedral form was determined rather late by Lipson and Stokes [8].

The main structural difference between amorphous carbon and graphite is due to their different sizes of ordered domains and not in the arrangement of atoms within these

domains. The concept of the crystallite size as the main cause of the line broadening in amorphous carbons has been predominant in most of the early works.

The gradual transition from the random layer structure to the graphite lattice was first interpreted quantitatively by Franklin [9] and in a somewhat different way by Houska and Warren [10].

Many workers, such as Hofmann and Wilm [11] and Bacon [12,13] have published information on the variation with crystalline size of the interlayer spacing of graphite. Franklin [9], in her studies of both non-graphitic and graphitic carbons, concludes that the measured interlayer spacing are really only mean values. She suggests that to a first approximation, the groups of oriented and disoriented layers in a graphitic carbon retain respectively the spacings of 3.354 Å and 3.44 Å, which are characteristics of highly crystalline graphite and non-graphitic carbon.

In the present investigation an attempt has been made to study inter layer spacing, Miller indices, relative intensity and integral widths of the diffraction lines by X-ray diffractometer of simple aromatic compounds with $AlCl_3$ as additives. By these parameters, we can assess the degree of graphitization.

2. Experimental

2.1. Sample preparation :

Contrary to the normal technique of preparing pure carbons by heating organic materials close to the graphitization temperature, this is done at relatively low temperature from the organic aromatic samples anthracene and phenanthrene, both without and with $AlCl_3$ as catalyst in different mole ratios. These substances are carbonized partially by heating to 400°C and 420°C respectively for 4 hours by scaled tube technique using solenoidal tubular furnace. The resulting carbons are studied by X-ray diffraction.

The samples were crushed into fine powder by using pestle and mortar. The sample on a glass slide was then placed into the diffractometer (Model No JDX-8P, JEOL Co. Ltd., Tokyo, Japan). Different diffraction patterns are obtained by using an automatic recorder. The parameters [14] used for the identification of the composite samples are :

(i) The spacing between the phases of atoms in the crystals '*d*',

(ii) The intensities of the X-ray reflections from the corresponding phases '*I*',

(iii) The Miller indices (*hkl*) values and

(iv) The integral width of the diffraction lines '*W*'.

3. Results and discussion

In the graphitic carbon, the extent of ordering associated with increasing order of graphitization can be estimated from X-ray diffraction pattern. Whatever be the degree of graphitization, diffuse bands can be identified. These diffused bands have angular positions that correspond roughly to the respective diffractive lines of the graphite (001, 002, *etc*) [Figures 1 and 2].

The intermediate stage, between disordered state of non-graphitic carbon and the ordered state of graphite, can be thought of as small layers of graphite-like structures which are stacked in parallel groups but not mutually oriented. From the shape of the diffused bands that correspond to the spectral lines of indices (*hkl*) of ordered graphite we can estimate the extent of ordering [9].

In an attempt to produce an alternating structure, the variation of the apparent interlayer spacing with the degree of graphitization in the graphitizing carbons and its

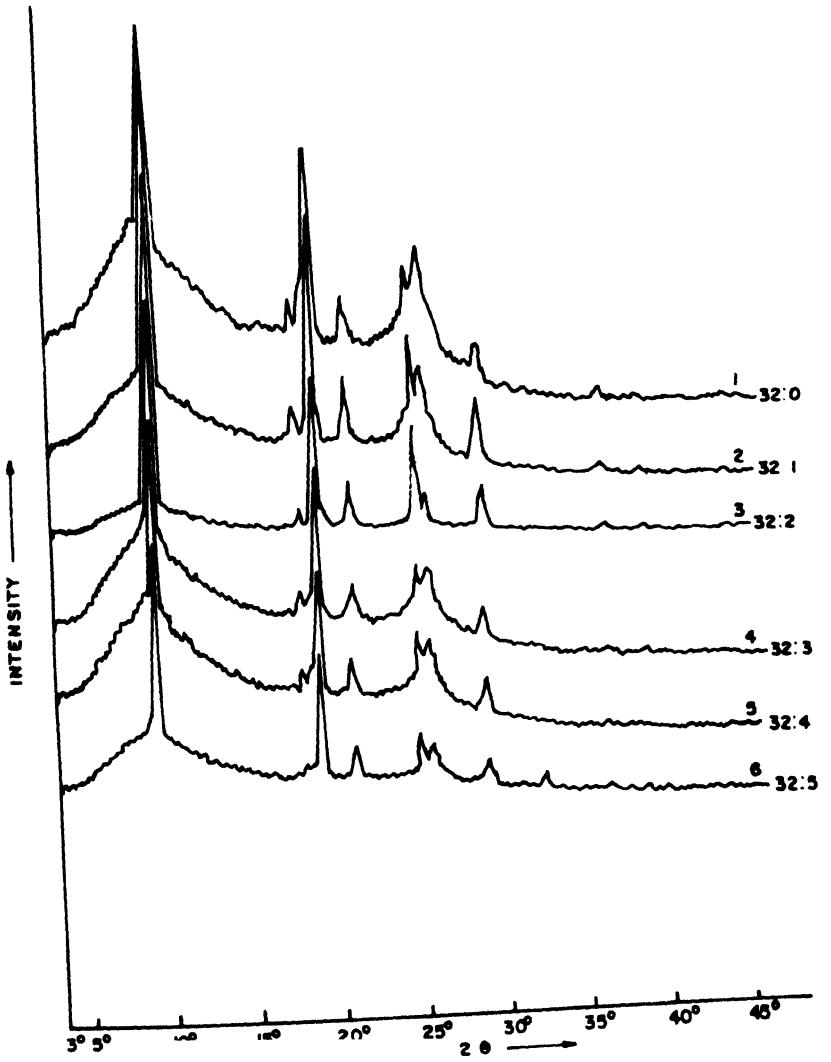

Figure 1. Intensity patterns of XRD of carbonised composite samples comprising of anthracene and $AlCl_3$ in different proportions.

constancy in both the non-graphitic carbons and in graphite, the different shapes of (001), (002), (003) and (004) lines and the apparent interlayer spacings, are to be taken into account.

The effect of catalytic agent ($AlCl_3$) on the graphitizing tendency is investigated from the shape of the bands [15,16]. It is observed that with increasing amount of $AlCl_3$, the sharpness of the diffraction lines (*hkl*) increases, the areas under the peaks representing the

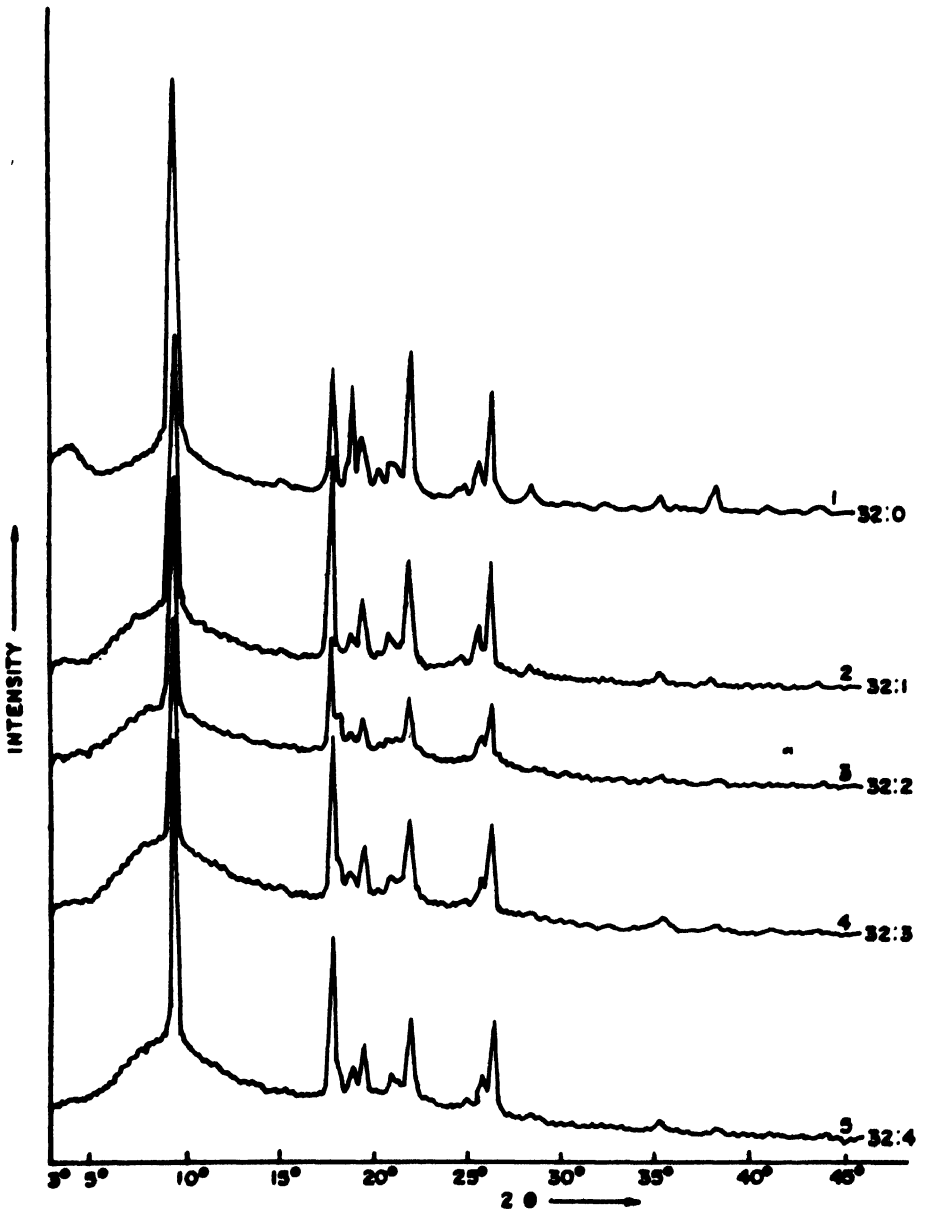

Figure 2. Intensity patterns of XRD of carbonised composite samples comprising of phenanthrene and $AlCl_3$ in different proportions.

number of atoms contributing to the scattering of X-rays and the widths of the peaks representing the radii of the spheres within which the atoms are distributed.

Since the magnitudes of widths of different peaks are different, the estimation of the widths of the peaks are made by taking the ratios of the area under each peak by the corresponding height. Representative data of crystallographic parameters of composite samples from anthracene are shown in the following table (Table 1).

Table 1. Crystallographic parameters of composite samples from anthracene.

Sample	No. of obs.	Angle (2θ) in degree	d in Å	Relative intensity	hkl	width (W) in mm
32 : 00	1	9.65	9.1544	100	001	4.14
	2	18.15	4.8818	2	002	0.67
	3	19.30	4 5934	16		1 06
	4	21.25	4 1761	4		1.11
	5	25.02	3.5547	10		1 54
	6	25.90	3.4359	16	003	1.97
	7	29.21	3.0537	4		1.23
	8	36.65	2 4490	1	004	1.33
32 : 1	1	9.72	9 0886	100	001	2.33
	2	18.20	4.8685	5	002	1.09
	3	19.41	4 5677	25		0.88
	4	21.35	4 1568	7		0.89
	5	25.30	3.5160	16		1.14
	6	25.95	3 4294	8	003	0.78
	7	29.35	3 0394	7		1.00
	8	36.75	2 4426	2	004	1.00
32 : 2	1	9.75	9.0607	100	001	1.34
	2	18.30	4.8422	3	002	0.64
	3	19.40	4.5700	26		0.78
	4	21.40	4 1472	7		0 70
	5	25.40	3.5024	19		0.54
	6	26.00	3.4229	6	003	0.71
	7	29.42	3.0324	9		0.88
	8	36.90	2.4330	1	001	0 60

The (*hkl*) lines become sharper as the degree of graphitization increases which is associated with the increase in the number of oriented layers. Sharpening of the bonds corresponds to the reduction of the radii of the spheres within which the atoms are distributed. The diffraction data, therefore, indicates a trend towards graphitization with increasing amount of the catalytic agent. This is in agreement with the observations made using DTA and TGA [17] and IR spectroscopy.

4. Conclusion

While the interlayer spacing is constant at 3.44 Å in the non graphitic carbons and at 3.354 Å in graphite, the apparent inter-layer spacing in the graphitic carbons decreases with increasing graphitization. This apparent interlayer spacing is in reality a mean value. In all graphitic carbons, whatever be the degree of graphitization, the small groups of orientated and disorientated layers within the parallel layer packets retain certain structural characteristic of crystalline graphite and of the non-graphitic carbons respectively. Among the orientated layers, the interlayer spacing is constant and is always equal to that in graphite, which is 3.354 Å.

The structure of the graphitic carbons is the simplest which is found to be consistent with all the experimental results. We can see that the interlayer spacing decreases with the increasing amount of catalyst. This indicates an increase in magnitude of graphitizability. Measurements of the width of different diffraction lines show that there is a mixture of at least two interlayer spacing in the graphitic carbons. We are, therefore, led to the conclusion that the graphitic carbons contain a mixture of oriented and disoriented layers, the spacing of the latter being greater than that of the former.

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